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# The reduction and control technology of tar during biomass gasification/pyrolysis: An overview

Jun Han, Heejoon Kim*

*Department of Ecological Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, 441-8580, Japan*

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**Abstract**

Biomass is an important primary energy source as well as renewable energy source. As the most promising biomass utilization method, gasification/pyrolysis produces not only useful fuel gases, char and chemicals, but also some byproducts like fly ash, $NO_x$, $SO_2$ and tar. Tar in the product gases will condense at low temperature, and lead to clogged or blockage in fuel lines, filters and engines. Moreover, too much tar in product gases will reduce the utilization efficiency of biomass. Therefore, the reduction or decomposition of tar in biomass derived fuel gases is one of the biggest obstacles in its utilization for power generation. In this paper, we review the literatures pertaining to tar reduction or destruction methods during biomass gasification/pyrolysis. On the basis of their characteristics, the current tar reduction or destruction methods can be broadly divided into five main groups: mechanism methods, self-modification, thermal cracking, catalyst cracking and plasma methods.


*Keywords:* Biomass; Gasification; Tar; Reduction or destruction

**Contents**



*Corresponding author. Fax: +81 532 44 6929.
*E-mail address:* kim@eco.tut.ac.jp (H. Kim).

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## 1. Introduction

It is well known that biomass is one of the important primary and renewable energy sources. Moreover, biomass is neutral in carbon dioxide circulation, that is, the amount of carbon dioxide it consumed through photosynthesis is the same as that given off by combustion. With the depletion of fossil fuel sources as well as the global warming issues, the utilization of biomass has been more and more concerned. At present, biomass share in world's total primary energy consumption is about 12%, as shown in Fig. 1. It is estimated that biomass share will be increased to near 15% by 2010 in developed countries [1].

The gasification/pyrolysis for producing syngas is regarded as one of the most promising options for utilizing biomass. The syngas from biomass can be not only directly used in gas turbine for power generation but also catalytically converted into methanol, dimethylether, Fischer–Tropsch oils or other chemical products.

In the gasification/pyrolysis process, with exception of generating useful products, many byproducts such as fly ash, $NO_x$, $SO_2$ and tar are also formed. Tar derived from biomass gasification or pyrolysis will be condensed as temperature is lower than its dew point, then block and foul process equipments like fuel lines, filters, engines and turbines. It was reported that tar content in the syngas from an air-blown circulating fluidized bed(CFB) biomass gasifier was about 10 g/m$^3$. For other types of gasifier, tar content varied from about 0.5 to 100 g/m$^3$ [2–5]. However most applications of product gases require a low tar content, of the order 0.05 g/m$^3$ or less. Hence, tar disposal becomes one of the most necessary and urgent problems during biomass gasification. Up to now, a great amount of

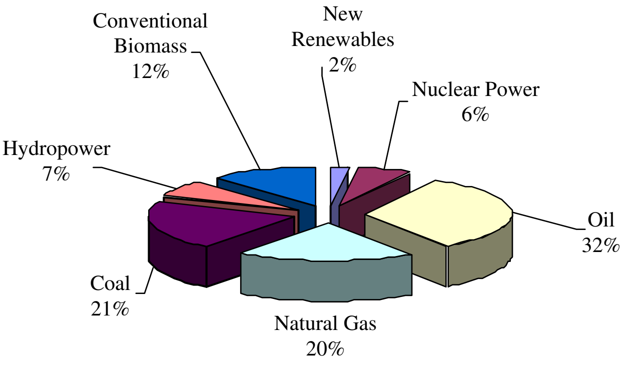


Fig. 1. The shares of current world's primary energy consumption.

work concerning tar reduction or reforming has been reported. In this work, we reviewed a great amount of literature and broadly divided the tar removal technologies into five groups: mechanism methods like cyclone, filters(baffle, fabric, ceramic), granular beds, RPS, Electrostatic precipitators and Scrubbers; self-modification, selecting optimal operation parameters for gasifier or using a low tar gasifier; Catalytic cracking; Thermal cracking and Plasma methods(Pyroarc, Corona, Glidarc).

## 2. Mechanism methods

Mechanism methods include scrubber, filter, cyclone and electrostatic precipitator. The primary use of these devices is to capture particles from the product gases. A great amount of experimental results demonstrated that the methods were also considerably efficient in removing tar accompanied with effective particles capture. Tar separation efficiency ranging from 51% to 91% had been reported in a venturi scrubber used to purify the product gases from a countercurrent rice husk gasifier [6]. Bridgwater [7] claimed that tar concentration in the fuel gases was lower than 20–40 mg/Nm$^3$ after a high-efficient scrubber system.

Except for venturi scrubber, other scrubbers such as water scrubber and wet scrubber are also widely used and proven as an effective removal technology for particulates, tar and other contaminants. It was reported that tar levels down to 20–40 mg/m$^3$ and particulate levels down to 10–20 mg/m$^3$ can be achieved with a water scrubber [8]. Dinkelbach [9] also reported 60% of tar can be removed from the raw gases by wet scrubbing in a CFB gasifier. Nevertheless, these systems are fairly expensive. Moreover, the mechanism methods only remove the tar from product gases, while the energy in the tar is lost. Especially, the systems generate a lot of contaminated water, which induces another waste disposal problem. To overcome the shortcoming, few attempts have been made to scrub the product gases with oil instead of water. However, the operating cost problem becomes more serious.

A so-called RPS(rotating particle separator) was used in Energy Research Center of Netherlands(ECN) with an attempt to remove tar from product gases, but the results was unsatisfactory [10]. Another new tar removal system called OLGA(“OLGA” is the Dutch acronym for oil-based gas washer) was also developed by Boerrigter in ECN [10], the outline of the system was shown in Fig. 2. The OLGA had been successfully demonstrated in a laboratory scale biomass gasifier. The results indicated that tar could be selectively removed from the product gases without affecting the main gaseous products like $C_2H_4$, $CH_4$, CO, and $H_2$. In the OLGA, heavy tars were completely removed, which resulted in the dew point decrease, even lower than 25 °C. Therefore, tar would not condense at the downstream of gasifier. Furthermore, 99% phenol and 97% heterocyclic tars removal can be achieved, which was expected to be high enough to prevent excessive waste water treatment cost due to the pollution with phenol or other water-soluble tar compounds.

Electrostatic precipitation(ESP) is one of the primary particle collection devices in coal fired power plant, metallurgical industry and cement industry due to its high efficiency. Paasen [11] declared that more than 99% dust and 40–70% tar removal can be obtained by the ESP at an updraft gasifier in Harboore, a downdraft gasifier at Wiener Neustadt and a circulating fluidized bed gasifier at ECN. After passing ESP, the heavy tars in product gases were completely removed and the dew point of tar ranged from 130 to 21 °C, which

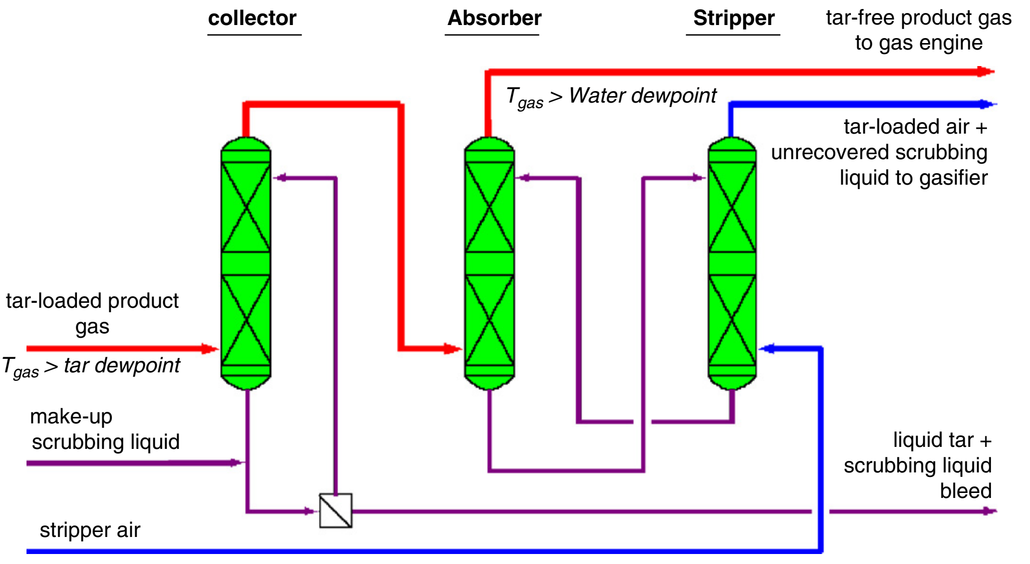


Fig. 2. The outline of OLGA process.

was sufficiently low for preventing the condensation of tar. Based on visual inspection, the author claimed that fouling at the ESP collector plates was negligible. Moreover, it was found that tar removal was not sensitive to the voltage and residence time.

Dinkelbach [9] also experimentally studied wet ESP used in a Wellmann gasifier in Birmingham (UK). In the system, no operation problem had been found for a long term and the operators claimed to have obtained good "tar" separation efficiencies. Unfortunately, no detailed experimental data was available in the paper. The validity of ESP capturing tar was also confirmed by Neeft [12].

Activated carbon is a highly efficient sorbent, and is widely used to control a number of gaseous pollutions emission. Hasler [6] investigated the possibility of using activated carbon granular bed filter to remove tar. The activated carbon filter was installed in the front of a fabric filter. In the experiments, the removal efficiencies for high boiling hydrocarbons and phenols were relative high. Meanwhile, the 'tar' laden activated carbon can be recycled as an extra feedstock. Hermann [14] studied a pre-coated fabric filter used to remove particles and tar at a gasifier plant in Austria. The filter had been tested for more than 2500 h without any problems. The disadvantages of the filters were the following: the tar deposited in filter could not be easily cleaned; tar accumulation on the filter surface would lead to eventual plugging. Generally, barrier filters were not suitable for tar removal even though the filters were successfully demonstrated in some cases.

Hasler [15] summarized the tar and particle reduction efficiency by various mechanism methods in Table 1.

## 3. Self-modification

As we know, the operating parameters play a very important role in the distribution of products during biomass gasification. The important parameters include temperature,

Table 1
The reduction efficiency of particle and tar in various gas cleaning system

| | Particle reduction (%) | Tar reduction (%) |
|---|---|---|
| Sand bed filter | 70–99 | 50–97 |
| Wash tower | 60–98 | 10–25 |
| Venturi scrubber | | 50–90 |
| Wet electrostatic precipitator | >99 | 0–60 |
| Fabric filter | 70–95 | 0–50 |
| Rotational particle separator | 85–90 | 30–70 |
| Fixed bed tar adsorber | | 50 |

equivalence ratio (ER), the type of biomass, pressure, gasifying medium and residence time etc. Certainly, the selection of parameters also depends on the type of gasifier.

Researchers have conducted extensive studies concerning the influence of temperature on tar production during biomass gasification [1,16–23]. Li [1] reported that tar yield from biomass gasification decreased drastically from 15 to 0.54 g/Nm$^3$ as the average temperature increased from 970 to 1090 K. NarvPaez [24] also studied biomass gasification at different temperatures and found that the tar content at 700 and 800 °C were 19 and 5 g/Nm$^3$, respectively. In the experiments of Fagbemi [16], tar yield was increased with the enhancement of temperature until to 600 °C, and then dropped with temperature increment. The phenomena can be explained the reasons: when the temperature was higher than 600 °C, the secondary reaction(i.e. tar cracking) prevailed, which leaded to tar decomposition.

Similar to temperature, Equivalence ratio(ER) increase also has a beneficial effect on reducing tar formation. However, the heat value of product gases will decrease with enhancing ER [20–22,25]. Lv [20] divided the biomass gasification into two stages based on the ER. In the first stage, ER varied from 0.19 to 0.23. When ER shifted from 0.19 to 0.23, gas yield also was increased from 2.13 to 2.37 Nm$^3$/(kg biomass) and gas low heat value(LHV) was increased from 8817 to 8839 kJ/Nm$^3$. The ER range of the second stage was 0.23–0.27. In the stage, gas LHV decreased with ER increment because of strengthening oxidization reactions of product gases. Garca-Ibanez [22] reported that the maximum amount of $H_2$ (9.3 vol%) occurred at an ER of 0.59 and ER had slight effect on the hydrocarbons content at the ER range of 0.59–0.73.

Kosstrin [26] investigated the relation of maximum tar yield with the type of biomass through experiments. It was obtained that the highest yield of tar was 35% for wood, around 60% for paper and only 30% for sawdust. A similar research was also conducted by Sadakata [27], who studied the conversion of wood, lignin and holocellulose at a heating rate exceeding 1000 °C/min. The maximum tar yield obtained by holocellulose was higher than that of other materials. While Toshiaki [19] stated that the tar yield from the three materials followed the sequence: xylan > Cellulose > lignin.

Devinder [28] described the effect of steam content on tar formation during biomass gasification through a thermodynamic model. The simulation predicted that the more steam, the higher is the conversion efficiency of tar. Turn, Zainal and Lv [20,21,29] also declared that the CO and $H_2$ fraction in product gases increased with steam/carbon ratio enhancement.

Knight [30] carried out biomass gasification under different pressures. Phenol was completely eliminated when the pressure was above 21.4 bar. However, the fraction of PAH increased with enhancing pressure though total tar decreased.

Besides affecting the fraction of tar during biomass gasification, operation parameters also influenced the tar properties. Paasen [4] revealed that tar concentration decreased with temperature varying from 750 to 950 °C. Simultaneously, tar compositions shifted from alkyl-substituted poly-aromatic hydrocarbons(PAHs) to non-substituted PAHs.

Yu [31] pyrolysed birch wood in a free-fall reactor to observe the temperature effect on the gasification process. He found that the amount of substituted 1- and 2-ring aromatics drastically went down with increasing temperature, and 3- and 4-ring aromatics yield was increased accordingly. Brage [32] reported an almost complete reduction of phenol content, 50% decrease in toluene content can be obtained when the temperature was raised from 700 to 900 °C. However, benzene and naphthalene had inverse tendency, their contents varied from 14 to 24 mg/l and 2 to 8 mg/l, respectively.

Gil [33] also investigated the impact of temperature on the composition of tar samples obtained from steam cracking of wood at 700–900 °C. He listed the compositions and concentration of tar at 700, 800 and 900 °C, respectively, as shown in Table 2. It can be seen that phenol, cresols and toluene were predominant at 700 °C, while naphthalene and indene were the major components at 900 °C.

Table 2
Effect of temperature on distribution of major organic tar compounds(g/kg dry wood)

| Analyte | 700 (°C) | 800 (°C) | 900 (°C) |
|---|---|---|---|
| Phenol | 1.069 | 0.941 | 0.753 |
| *o*-Cresol | 0.929 | 0.737 | 0.300 |
| *m*-Cresol | 1.140 | 0.917 | 0.503 |
| *p*-Cresol | 0.739 | 0.545 | 0.276 |
| 2,5-Xylenol | 0.340 | 0.303 | 0.137 |
| 3,4-Xylenol | 0.260 | 0.184 | 0.077 |
| 2,6-Xylenol | 0.260 | n.d | 0.174 |
| *o*-Ethylphenol | 0.353 | 0.381 | 0.240 |
| Toluene | 1.125 | 0.274 | 0.538 |
| *o*-Xylene | 0.580 | 0.356 | 0.653 |
| Indene | 0.649 | 0.628 | 1.425 |
| Naphthalene | 0.345 | 0.494 | 1.722 |
| 2-Methylnaphthalene | 0.242 | 0.277 | 0.456 |
| 1-Methylnaphthalene | 0.164 | 0.187 | 0.289 |
| Biphenyl | 0.044 | 0.053 | 0.125 |
| Acenaphthylene | 0.208 | 0.285 | n.d. |
| Fluorene | 0.119 | 0.149 | 0.276 |
| Phenanthrene | 0.065 | 0.100 | 0.368 |
| Anthracene | 0.017 | 0.042 | 0.107 |
| Pyrene | 0.049 | 0.038 | 0.140 |
| Pyridine | 0.168 | n.d. | n.d. |
| 2-Picoline | 0.041 | n.d. | n.d. |
| 3-Picoline | 0.027 | n.d. | n.d. |
| 2-Vinylpyridine | 0.054 | n.d. | n.d. |
| Quinoline | 0.055 | n.d. | n.d. |
| Isoquinoline | 0.014 | n.d. | n.d. |
| 2-Methylquinoline | 0.009 | n.d. | n.d |

Based on the molecular weight of tar compounds, some researchers [34–37] divided tar components into five groups, as shown in Table 3. They discovered that temperature increase had a positive effect on the decomposition of class 1 and class 2 tars, while class 3 and class 5 tars concentration increased with temperature enhancement.

Sousa [37] performed tests to study how ER affected tar formation during wood gasification. The experimental results showed that the tar was a complex mixture of polycyclic aromatic compounds (benzene making 25% of the tars by mass, naphthalene 5.1%, indene 4.9%, acenaphthylene 1.7% and phenanthrene 1.4%), alkylated aromatic compounds (toluene 13.6%, styrene 5.3% and xylenes 5.2%) and phenolic compounds (phenol 15.1%, cresols 11.1%) at $ER = 0.2$. When ER was increased to 0.3, the composition became less complex. The primary component was polycyclic aromatic compounds(benzene 42.9%, naphthalene 14.7%, indene 5.2%, acenaphthylene 4.4% and phenanthrene 3.9%), and the concentrations of alkylated aromatic compounds decreased remarkably. As for phenolic compounds, cresols completely disappeared and only a small amount of phenol was detected. At $ER = 0.4$, the tar was decomposed almost exclusively of benzene(60% of the tars by mass), naphthalene (17%) and a small amount of three and four ringed polycyclic aromatic hydrocarbons. Contrary to Sousa, Houben [38,39] reported that increasing ER led to the formation of higher ring aromatic components.

Tregrossi [41] experimentally studied rich tar premixed flames burned at different C/O ratios. On the basis of results, he concluded that increasing ER ($\lambda$) induced in more higher ring aromatic components formation, as shown in Fig. 3. The effect of residence time was also evaluated by Tregrossi, the results can be seen in Fig. 4.

The type of gasifer is another important parameter affecting the yield of tar. Morf [42] reviewed the tar content in different gasifiers and summarized the mean tar content in Table 4. As seen in Table 4, cocurrent fixed bed was the best effective method in suppressing the formation of tar during biomass gasification.

Technical University of Denmark developed a two-stage gasifier in 1980–1990, the tar content in the product gases was extremely low, below $25\,mg/Nm^3$. After passing the gas cleaning device (particle filtration), the tar content was even about $5\,mg/Nm^3$ [43], while average tar content in the product gases from conventional downdraft gasifiers was $58\,mg/Nm^3$. In the two-stage gasifier, the pyrolysis and gasification processes were separated into two different zones. In the zones between pyrolysis and gasification, the volatiles from the pyrolysis zone were partially oxidized. Hence, most of the tar was able to be decomposed into gases.

Table 3
Classification of tar components

| Group | Name | Composition |
|---|---|---|
| Class1 | GC-undetectable | Determined by subtracting the GC-detectable tar fraction from the total gravimetric tar. |
| Class 2 | Heterocyclic aromatics | Pyridine, phenol, cresol, quinoline |
| Class 3 | Aromatics (1 ring) | Xylene, styrene, toluene |
| Class 4 | Light PAH compounds (2–3 ring) | Naphthalene, biphenyl, acenaphtylene, fluorene, phenanthrene, anthracene |
| Class 5 | Heavy PAH compounds (4–7 ring) | Fluoranthene, pyrene, chrysene, benzo - fluoranthene, benzopyrene, perylene |

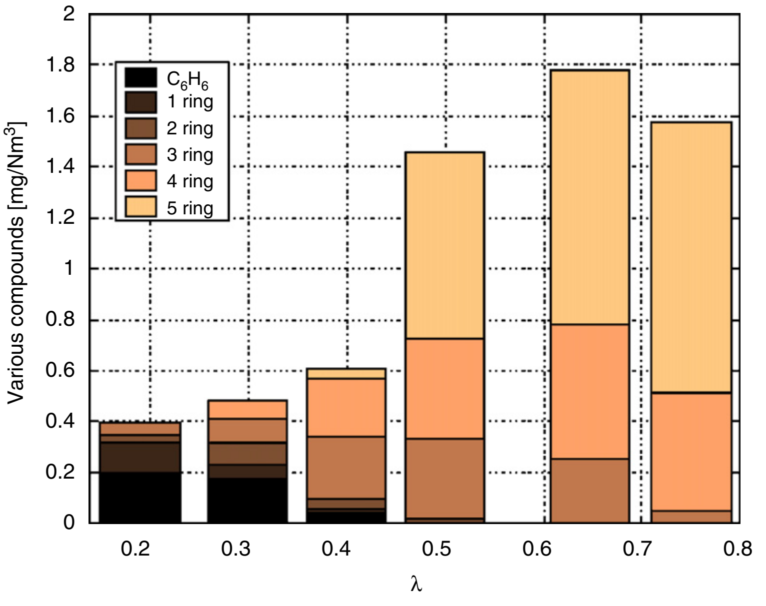


Fig. 3. The effect of ER($\lambda$) on the tar oxidation.

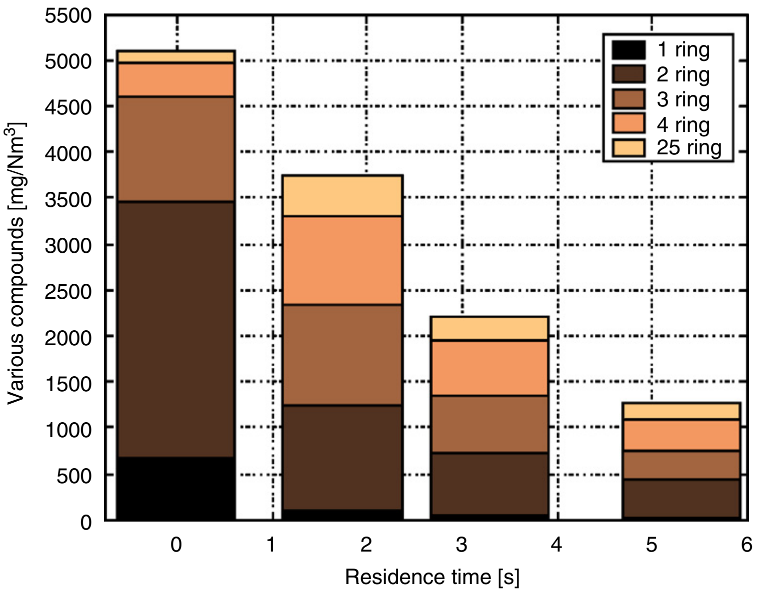


Fig. 4. The effect of residence time on tar oxidation.

A two-stage wood gasification process had also been studied at the Asian Institute of Technology(AIT), Thailand [44]. Using the gasifier, the fuel gases produced by biomass gasification only contained about 19–34 mg/Nm$^3$ tar.

Table 4
The tar content in different gasifier

| | Fixed bed | | Fluidized bed | |
|---|---|---|---|---|
| | Countercurrent | Cocurrent | Bubbling | Circulating |
| Mean tar content (g/Nm$^3$) | 50 | 0.5 | 12 | 8 |
| The range of tar (g/Nm$^3$) | 10–150 | 0.01–6 | 1–23 | 1–30 |

Table 5
Tar and soot in gas after cracking

| Temperature in reactor (°C) | 1200 | 1250 | 1290 | 1290 |
|---|---|---|---|---|
| Gas producer | Pyrolysis | Pyrolysis | Pyrolysis | Updraft |
| Light tar in condenser determined with GC/MS (mg/kg dry feed stock) | 670 | 21 | 1 | 7 |
| Light tar in aerosol filter determined with GC/MS (mg/kg dry feed stock) | 250 | n.d | 5 | 10 |
| Light tar in soot determined with GC/MS (mg/kg dry feed stock.) | n.d | n.d | n.d | 15 |
| PAH in condensate. Sum of 27 components (mg/kg dry feed stock.) | 19 | 0.021 | 0.033 | 0.07 |

## 4. Thermal cracking

In thermal cracking method, the raw gases derived from gasification or pyrolysis were heated to a high temperature, where tar molecules can be cracked into lighter gases [45–46]. Bridegwater [7] reviewed that tar could be reduced by thermal cracking in a fluidized bed gasifier. Meanwhile, the author also mentioned that biomass-derived tar was very refractory and hard to crack by thermal treatment alone. In order to effectively decompose the tar, the following ways were suggested: increasing residence time, such as using a fluidized bed reactor freeboard, but this method was only partially effective; Direct contacting with an independently heated hot surface, which required a significant energy supply and decreased the overall efficiency. At the same time, the method was also partly effective and depended on good mixing; Partial oxidation by adding air or oxygen could increase CO levels at the expense of conversion efficiency decrease and operation cost enhancement.

To achieve a sufficiently high tar cracking efficiency, Brandt [47] claimed that the necessary temperature and residence time were 1250 °C and 0.5 s, respectively. Tar and soot content at 1200, 1250 and 1290 °C are shown in Table 5. According to the review of Beenackers and Manuatis [48,49], the preferable tar content in gases for engine application was below 50 mg/Nm$^3$. Hence, 1250 °C was the limited temperature for tar decomposition.

Houben [38] also carried out thermal tar cracking experiment at temperature range of 900–1150 °C and residence time between 1 and 12 s. In the experiment, naphthalene carried by nitrogen was used as model tar. The maximal tar reduction reached 98–99% at 900 °C with an excess air ratio of 0.5.

## 5. Catalyst cracking

Due to the advantages of converting tar into useful gases and adjusting the compositions of product gases, catalyst cracking has been of interest since the middle 1980s. The simplified mechanism for catalyst tar reforming can be described as follows [50]. First, methane or other hydrocarbons are dissociatively adsorbed onto a metal site where metal-catalyzed dehydrogenation occurs. Water is also dissociatively adsorbed onto the ceramic support, hydroxylating the surface. At the appropriate temperature, the OH radicals migrate to the metal sites, leading to oxidation of the intermediate hydrocarbon fragments and surface carbon to $CO + H_2$. David[39] summarized the criteria for catalyst as follows:

1. the catalysts must be effective in removing tar;
2. if the desired product was syngas, the catalysts must be capable of reforming methane;
3. The catalysts should provide a suitable syngas ratio for the intended process;
4. the catalysts should be resistant to deactivation as a result of carbon fouling and sintering;
5. the catalysts should be easily regenerated.
6. The catalysts should be strong; and
7. the catalysts should be inexpensive.

Moreover, David reviewed tar catalyst cracking and divided the catalysts into three groups: dolomite catalysts; alkali metal and other metal catalysts; nickel catalysts. After several years of developing, some new catalysts have been applied in gasification. Here, we group the catalysts into four groups and detailed description can be found in the following.

## 6. Ni-based catalyst

Ni-based catalysts are extensively applied in the petrochemical industry for naphtha and methane reforming [50–65]. Meanwhile, a wide variety of Ni-based catalysts are commercially available. Especially, some studies showed that nickel based catalysts had the ability of reversing ammonia reaction, thus it is possible to reduce $NO_x$ emission during biomass gasification [50–52].

Zhang [57] investigated tar catalytic destruction in a tar conversion system consisting of a guard bed and catalytic reactor. Three Ni-ased catalysts (ICI46-1, Z409 and RZ409) were proven to be effective in eliminating heavy tars (>99% destruction efficiency). Hydrogen yield was also improved by 6–11 vol%(dry basis). The experimental results also demonstrated that space velocity had little effect on gas compositions, while increasing temperature boosted hydrogen yield and reduced light hydrocarbons ($CH_4$ and $C_2H_4$) formation, which suggested that tar decomposition was controlled by chemical kinetics.

Coll [61] also studied the model compounds like benzene, toluene, naphthalene, anthracene, and pyrene were cracked using two commercial nickel catalysts: UCG90-C and ICI46-1 at 700–800 °C. The order of these model tars reactivity was: benzene > toluene > anthracene > pyrene > naphthalene. Toluene conversion rate ranged from 40% to 80% with the ICI46-1 catalyst, and 20% to 60% for the UCI G90-C catalyst.

Simell and co-workers [66–69] reported the use of alumina and other catalysts with variable Ni content reformed toluene in various gas atmospheres at 900 °C and

0.5–20 MPa. The effects of sulfur poisoning on the activity of these catalysts for tar and ammonia decomposition had also been evaluated.

Nickel supported on silica was active for tar catalyst cracking at relatively low temperature(823 K) was described by Zhang [70]. However, these catalysts only maintained their activities for a short time because of accumulating large amounts of carbon on their surfaces. Aznar [71] and Baker [72] also mentioned the phenomena in their experiments. In order to overcome the shortcoming of the commercial Ni-based catalyst, many Ni-based catalysts were developed.

Dou [61] compared five catalysts on tar removal from fuel gases in a fixed-bed reactor. The Y-zeolite and NiMo catalysts were found to be the most effective, such that 100% tar removal can be achieved at 550 °C. It was also observed that process variables like temperature and space velocity had very significant effect on tar removal. The visual observation demonstrated that only very small amount of coke appeared at the surface of catalyst even with 168 h operation. The result of Mariño [73] indicated that the addition of Ni into $Cu/Ni/K\gamma–Al_2O_3$ catalyst was favorable to gases yield increase and acetic acid production reduction during ethanol gasification.

Magnesium, lanthanum, and titanium oxide-doped nickel–chromium/alumina catalysts were prepared by Denis [74], and experiments were performed to assess the performance of these catalysts in steam reforming naphthalene. The experimental results revealed that the improved catalyst could promote conversion efficiency of naphthalene. After the structure analysis, it was found that MgO had a significant effect on the robustness of catalyst due to the formation of $MgAl_2O_4$ spinel phase.

Courson [75–77] also developed a new Ni–based catalyst by impregnating nickel oxide on olivine and calcination at 900, 1100 and 1400 °C. X-ray diffraction, scanning electron microscopy and transmission electron microscopy coupled to energy dispersive X-ray spectroscopy analysis showed that there were interactions between the precursor and the support, which was consistent with the conclusion of Denis. After the characteristic studies, the catalyst performance tests indicated that the catalyst containing 2.8 wt% Ni calcined at 1100 °C was the optimum catalyst. Furthermore, no sintering and very little carbon deposition were observed on this catalytic surface.

Chen [78] investigated $CO_2$ reforming methane over $NiO/\gamma–Al_2O_3$ catalyst in a fixed/fluidized bed. Francisco [79] also compared the Ni catalyst supported on $\alpha$-$Al_2O_3$, $ZrO_2$ and $\alpha$-$Al_2O_3$–$ZrO_2$, and found $Ni/\alpha–Al_2O_3–ZrO_2$ catalyst showed better performance. In the literature of Karen [80], he mentioned that the 1 wt%/0.5 wt% nickel/calcium catalyst co-precipitated inside porous filter discs can effectively remove tar(>98%) even in the presence of 100 ppm $H_2S$.

## 7. Alkali metal catalysts

Besides Ni–based catalysts, many literatures proved that alkali metal catalysts were also effective in reforming tar [51,81–84]. McKee [83] successfully demonstrated that carbonates, oxides and hydroxides of alkali metals can effectively decompose tar during catalytic gasification.

Gong [82] also studied waste paper gasification in carbon dioxide atmosphere with molten alkali metal carbonates including potassium, sodium, lithium carbonate or their intermixtures as catalyst. The molten catalysts were capable of facilitating a desired reaction($C + CO2 \rightarrow 2CO$), which was hardly feasible even at a high temperature of 973 K

without catalysts. Further experimental results demonstrated that the intermixed carbonates exhibited stronger enhancement on catalytic ability than any carbonate salts in pure form. Waste paper gasification catalyzed by molten alkali carbonates was also investigated by Roman [84].

In the experiment of Demirba [85], three different biomass samples (cotton cocoon shell, tea factory waste and olive husk) were decomposed by direct and catalytic pyrolysis process to obtain hydrogen rich gaseous products at 775, 925, 975 and 1025 K. In the catalytic pyrolysis process, the yield of hydrogen rich gases was increased in the case of using $ZnCl_2$ catalyst though the yield of charcoal and liquid products were also increased. While the effect of $K_2CO_3$ and $Na_2CO_3$ on pyrolysis products depended on the biomass species. It was found that the $Na_2CO_3$ was better than $K_2CO_3$ for the cotton cocoon shell and tea factory waste pyrolysis. Nevertheless, in the case of olive husk pyrolysis, the conclusion is opposite, and $K_2CO_3$ was more effective than $Na_2CO_3$. At the same time, the effect of the amount of $Na_2CO_3$ and $K_2CO_3$ on the pyrolysis products was irregular.

Pant [86] and Kumar [87] also pyrolysed *n*-heptane over different calcium aluminates and potassium impregnated calcium aluminate in a fixed bed reactor. Compared to the unpromoted catalysts, $K_2CO_3$ impregnated catalyst significantly suppressed the coke deposited on the catalyst surface, but only had marginal effect on the product selectiveness. Brown [88] also found alkali metal salts, especially those containing potassium, were excellent promoters for gasification reactions. On the contrary to the conclusion of Brown, a gravimetric study of the alkali metal hydridotetracarbonyl-ferrates catalytic activity at 800 °C revealed the following sequence with respect to the cation activity: $Na > Li > K > Rb > Cs$ [89].

## 8. Dolomite catalysts

Dolomite is a calcium magnesium ore with general chemical formula $CaMg\ (CO_3)_2$, and is generally used as raw material in the manufacture of magnesium. In recent years, it has been discovered that calcined dolomite is also a highly efficient catalyst for removing tar from the product gases of gasifier.

Simell [65] compared a commercially available metal based catalyst($NiMo/\gamma–Al_2O_3$) with non-metallic mineral catalysts during the catalytic pyrolysis of toluene. The non-metallic mineral catalysts included Norwegian dolomitic magnesium oxide [MgO], Swedish low surface quicklime[CaO], and calcined dolomite [$CaMg(O)_2$]. Among these catalysts, the catalytic effect followed the sequence: $CaO > CaMg(O)_2 > MgO > NiMo/\gamma–Al_2O_3$.

Rui and Rapagn [90,91] claimed that the presence of dolomite in the fluidized bed had the benefit of decreasing tar content and rising gases yield. However, dolomite could not affect gaseous hydrocarbons concentrations. It was reported that an amount of 20–30 wt% dolomite(rest being silica sand) in the gasifier reduced tar content to about 1 g/m$^3$ at an ER of 0.3 [92]. The authors also studied the influence of several operating parameters combined with using in-bed dolomite.

Devi [93–95] reported that untreated olivine could convert only 46% tar in the hot gasification gases, which could not be considered as a significant reduction. While catalyst was pre-treated olivine, the conversion of naphthalene, considered as a model biomass tar compound, was as high as 80%. The pretreatment was only heating the olivine catalyst at 900 °C in the presence of air. It was expected that the calcination could activate olivine.

Karlsson [96] successfully demonstrated biomass integrated gasification with combined cycle (IGCC ) process with dolomite as bed material. Only about 1–2 $g/m^3$ of light tars(excluding benzene) and 100–300 $mg/m^3$ of heavy tars were detected in the product gases.

Srinakruang and Wang [97,98] developed a new catalyst (Ni supported by dolomite), which could maintain high activity and stability for a long contact time. Moreover, carbon deposition at the Ni/dolomite catalysts surface was negligible. The authors also claimed that the calcination temperature significantly influenced the property and activity of the Ni/dolomite catalyst since nickel oxide had strong interaction with the dolomite surface.

Although the dolomite can effectively remove tar in some cases, there are still many problems during biomass gasification. Zhang [99] reviewed the shortcomings of dolomite as the following: The conversion rate of tar catalyzed by dolomite was difficult to reach or exceed 90–95%; Although dolomite could reduce the tar in syngas and change the distribution of tar compositions, it was difficult to convert the heavy tars by dolomite; The dolomite would be inactive since the particle was easily broken during gasification; The melting point of dolomite was low and the catalyst would be inactive resulting from the melting of dolomite.

## 9. Novel metal catalysts

As described above, the Ni-based catalysts and dolomite were deactivated significantly by carbon deposition and alkali metal was easily sintered. Novel metals had been wildly used as catalyst for $NO_x$ and $SO_2$ since 1980s [100–102]. Some researchers found that the novel metal catalysts were able to overcome the shortcomings of conventional catalyst, and keep high efficiency on converting tar. Tomishige [103] compared the tar conversion rates over $M/CeO_2/SiO_2$ ($M = Rh$, Pd, Pt, Ru, Ni) catalyst during cellulose gasification. The order of catalyst activity in the cedar wood gasification at 823 K was the following: $Rh > Pd > Pt > Ni = Ru$. The tar conversion rate was about 88% in the case of $Rh/CeO_2/SiO_2$ catalyst at 823 K, which jumped to the 97% at 873 K. Since the amount of char on $Rh/CeO_2/SiO_2$ catalyst surface was very small at low temperature, no deactivation was observed during the operation period. In addition, $Rh/CeO_2/SiO_2$ exhibited high and stable activity even under the presence of high concentration of $H_2S$(280 ppm) [104].

Asadullah and coworker [2,105–110] also studied the performance of various kinds of $Rh/CeO_2/M$-type($M = SiO_2$, $Al_2O_3$, and $ZrO_2$) catalysts for cellulose gasification in a continuous-feeding fluidized-bed reactor. Among the catalysts, $Rh/CeO_2/SiO_2$ exhibited the best performance with respect to generating syngas or hydrogen. Moreover, Pt, Ru, Pd, and Ni doped on $CeO_2$, and supported by $SiO_2$, $Al_2O_3$, $TiO_2$, MgO, and $ZrO_2$ were also tested and the results also proved that $Rh/CeO_2$ was the best catalyst. However, in the continuous-feeding system, it was found that the $Rh/CeO_2$ catalyst suddenly deactivated due to a decrease in surface area from 60 to 13 $m^2/g$. After further study, the authors found that the loading of $CeO_2$ on the high-surface-area $SiO_2$ could inhibit the aggregation of $CeO_2$ and maintain the catalytic activity. Among various loadings, 35%wt $CeO_2$ on $SiO_2$ was the most suitable support for Rh in terms of the tar conversion, gas yield, and fast char conversion.

The catalytic performances of Co catalysts for the steam reforming of naphthalene were reported by Furusawa [59,111]. The characterizations analysis(TPR, XRD, CO adsorption, and CO-TPD) of catalysts showed that the large-sized Co metal particles were formed over the precalcined catalysts.

Hao [112] investigated Ru/C, Pd/C, $CeO_2$ particles, nano-$CeO_2$ and nano-$(CeZr)xO_2$ catalytic cracking tar during cellulose and sawdust gasification. The experimental results demonstrated that the catalyst activities followed the order: Ru/C > Pd/C > nano-$(CeZr)xO_2$ > nano-$CeO_2$ > $CeO_2$. Rh supported on $CeO_2$, $ZrO_2$ and $SiO_2$ single metal oxides and various mixed metal oxides such as $CeO_2/SiO_2$, $ZrO_2/SiO_2$ and $CeO_2/ZrO_2$ were compared by Polychronopoulou [113], and found that 1.5 wt% $Rh/CeO_2/ZrO_2$ catalyst, the support of which was prepared by the sol–gel method, exhibited better performance than other catalysts.

Sutton [114] also studied the activity of the 3:17 Ni/Al co-precipitated catalyst with 1 wt% $Ru/Al_2O_3$ and 1 wt% $Pt/ZrO_2$ for dry reforming $CH_4$ and $C_3H_8$ at 450–800 °C. Rapagna [115] developed a catalyst with a chemical formula of $LaNi_{0.3}Fe_{0.7}O_3$, which was prepared by means of a sol–gel related process, where La, Ni, and Fe nitrate salts were dissolved separately in hot propionic acid. The catalyst displayed high $CH_4$ reforming activity at 800 °C. Garcia[116] also reported that cobalt-promoted and chromium-promoted nickel catalysts supported on a $MgO–La_2O_3–\alpha\text{-}Al_2O_3$ performed the best in terms of $H_2$ yield and lifetime.

## 10. Plasma method

Several groups [117–121] successfully demonstrated that organic compounds were easily decomposed by corona discharges. The removal fraction for 300 ppm methane in atmospheric pressure air, with a residence time less than 0.5 ms, was measured at 80% with an energy density of 4 KJ/l. Experiments of Nair [122–125] had demonstrated that tars and particles can be removed simultaneously by plasma. In addition, the effect of temperature on naphthalene removal efficiency in a gas mixture of $N_2 + CO_2(10\%)$ was also discussed, as shown in Fig. 5.

At 400 °C, about 50% naphthalene was thermally decomposed at a time of 20 min. With corona discharge, 50% removal can be achieved with an energy density of 40 J/L at 400 °C in only about 3 min. It was assumed that this was due to the high-energy electrons created reactive species/radicals by way of collisions. The reaction was determined using background gas compositions, temperature and other factors:

| | |
|---|---|
| Radical production reaction; $k1$, | $M \rightarrow R$, |
| Tar removal reaction; $k2$, | $X + R \rightarrow A$, |
| Linear radical termination reaction; $k3$, | $M + R \rightarrow B$, |
| Non-linear radical termination reaction; $k4$, | $R + R \rightarrow B$, |

where $M$ is the background gas molecule, $R$ the radical created, $A$, $B$, $C$ intermediates.

At the same time, it was concluded that the increase of gas temperature may not only improve its related oxidation kinetics, but also improve the initial O radical yield via $O_2$ decomposition.

To investigate the reliability of the plasma system, field tests were also carried out on a wood gasifier [126], which was designed to produce a 100 kW electrical output. The results from the experiments showed dust removal efficiency of about 72–95%. As for tar, the conversion rates of heavy and light tar were 68% and −50%, respectively.

Pemen [127] also carried out an experiment to study tar removal in a 1 Kg/h biomass gasifier by gliding-arc method. The operating temperatures varied from 400 to 800 °C and

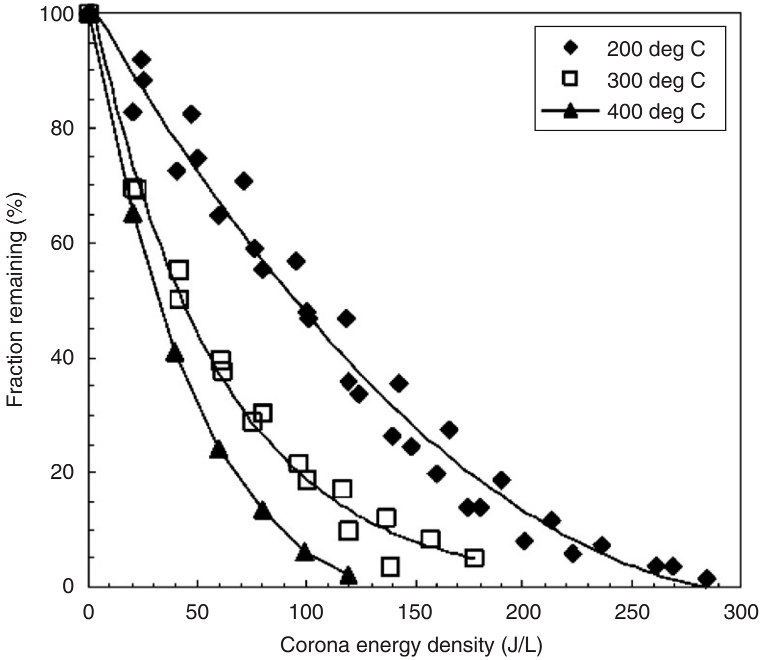


Fig. 5. Naphthalene removal from a gas mixture—Effect of temperature.

the applied energy densities varied between 0 and 1900 Kje/m$^3$. The following results were obtained:

1. The tar conversion increased slightly with increasing energy density.
2. The tar conversion increased continuously with increasing reactor temperature.

Besides effectively capturing tar and particle, plasma method has the following advantages: it can operate at a high temperature and be retrofitted to existing installation.

## 11. Conclusions

Although the primary use of mechanism methods is to capture the fly ash or particles from product gases, the effect on tar removal is also very good. About 40–99% tar can be reduced by the different mechanism methods such as water scrubber, venturi scrubber, cyclone, ESP and rotational particle separator. However, these methods only remove or capture the tar from product gases, while the energy in tar is lost. The self-modification and other methods can not only reduce the tar but also convert the tar into useful gases. The self-modification methods include: selecting better gasifer, and optimizing operation parameters. Tar reduced by modifying operation parameter is at the expense of reducing the heat value of gases. At present, a new two-stage gasifier can produce the syngas with low tar content and high heat value. Catalyst cracking, and thermal cracking are generally used to decompose or reduce tar though there are still some disadvantages. In order to get highly efficient tar decomposition, the temperature of thermal cracking needs to be very

high, which results in operating cost increase. Catalyst cracking can modify the composition of product gases at very low temperature. Nevertheless, there still exists shortcomings such as: the commercial Ni-based and alkali metal catalysts will be inactive by deposited carbon and $H_2S$, as for dolomite catalyst, broken particles also decrease the activity. The newly developed novel catalyst can overcome the disadvantages. Plasma technology cannot only effectively remove fly ash, $NO_x$ and $SO_2$, but also sharply decrease the formation of tar during biomass gasification.

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